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(54) Catalyst devices

(57) A device for use in the catalysis of a chemical reaction has a container (1) with a fluid inlet (5) thereto and a fluid outlet (6) therefrom and a number of catalyst bodies (8) assembled therein.

The catalyst bodies (8) are packed in the container (1) in a pre-determined orientation comprising one or more trains (7) thereof occupying the cross-section of the container (1). In order to reduce resistance to flow of reactants through the device, each of the catalyst bodies (8) has a plurality of internal channels of an ordered, pre-determined size and arrangement for permitting substantially unrestricted flow of reactants therethrough. Also, the or each train (7) is aligned with the general direction of flow of reactants through the device to define pathways for reactants to pass therethrough in this general direction. The catalyst bodies (8) each carry catalytically active material for the reaction.

Fig. 1.

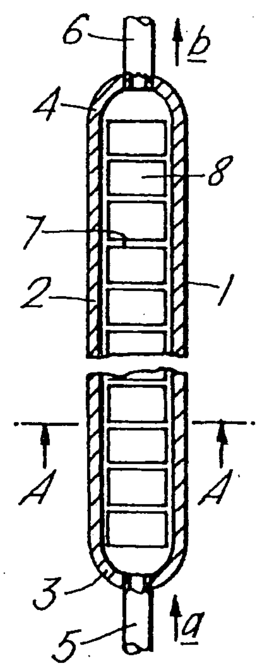

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Fig. 1.

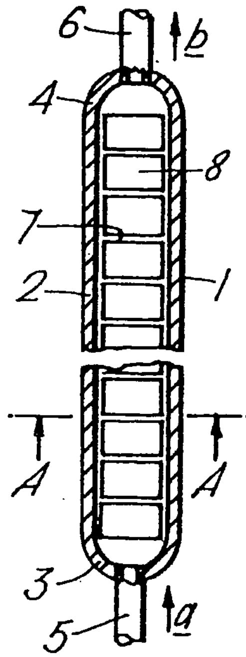
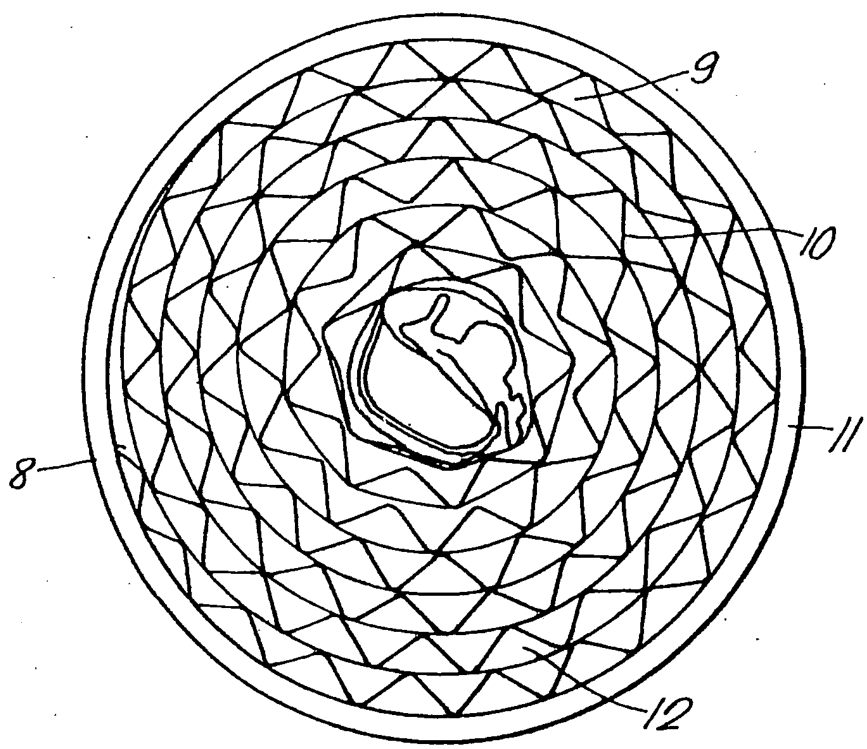


Fig. 2.



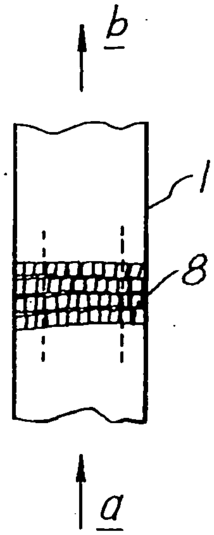


Fig. 3.

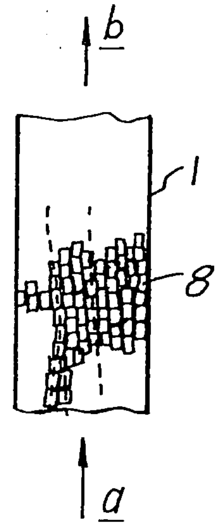


Fig. 4.

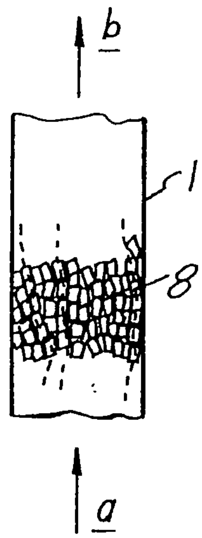


Fig. 5.

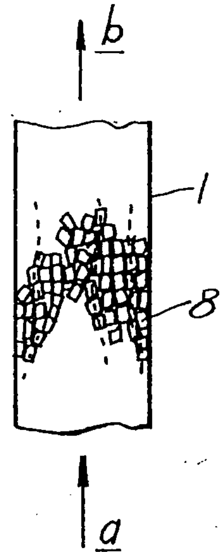


Fig. 6.

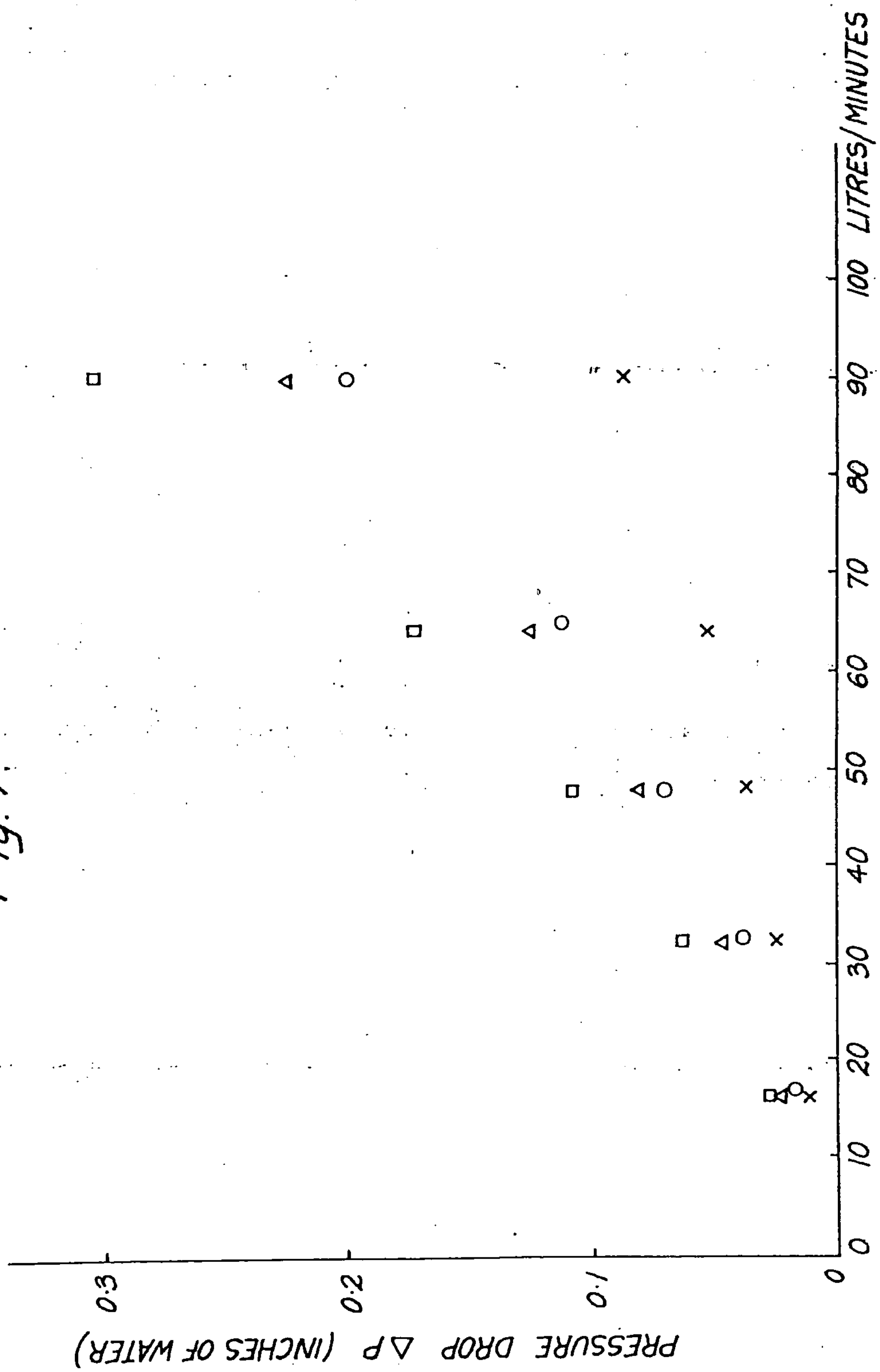

LITRES/MINUTES
0
10
20
30
40
50
60
70
80
90
100
PRESSURE DROP ΔP (INCHES OF WATER)
0
0·1
0·2
0·3

Fig. 7.

SPECIFICATION
Catalyst device

This invention relates to a device for use in the catalysis of chemical reaction comprising a container having a fluid inlet thereto, a fluid outlet therefrom and a plurality of discrete catalyst bodies assembled therein, each body carrying a surface coating comprising catalytically active material for the reaction, in operation of which fluid passes in a general direction of flow through the container from the inlet to the outlet.

Catalyst devices comprising a plurality of catalyst pellets randomly assembled in a container are well-known in the art. See, for example, "Chemical and Catalytic Reaction Engineering" by J. J. Carberry, published by McGraw-Hill (1976). Also, UK Patent Application Publication No. 2 053 957A describes carrying out certain chemical reactions in the presence of a catalyst supported on a metal or alloy resistant to the conditions in which the reaction is carried out. The catalyst support may be in a container and in the form of small, random-packed honeycombs.

There is always interest in improving the performance of catalyst devices and the invention as claimed is concerned with provision of catalyst bodies in certain ordered arrangement in catalyst devices thereby to attain improvement in performance.

The invention comprises a container having a fluid inlet thereto, a fluid outlet therefrom and a plurality of discrete catalyst bodies assembled therein, each body carrying a surface coating comprising catalytically active material for the reaction, in operation of which, fluid passes in a general direction of flow through the container from the inlet to the outlet, characterised in that each body has a plurality of internal channels of an ordered, pre-determined size and arrangement to permit substantially unrestricted flow of fluid therethrough, each body has an external protective boundary to protect the body from attrition, and the bodies are assembled in a pre-determined orientation comprising one or more trains occupying the cross-section of the container, the or each train and said channels of each body being aligned with said general direction of flow to define pathways for fluid to pass therethrough in said general direction.

The channels in the bodies of the invention may be substantially parallel with respect to one another and, in the case of a cylindrical body, may be parallel with respect to the principal axis of the cylinder. Other arrangements of channels may be possible, dependent upon manufacturing feasibility and the requirements of the device.

In operation of the device, a fluid reactant or reactants are passed via the fluid inlet into the container. The reactant or reactants pass through the channels in the bodies thereby contacting the catalytically active material which catalyses the chemical reaction. The fluid product or products of the reaction leave the container via the fluid outlet. The general direction of flow of fluid through the container may be downward or in any other direction as appropriate.

The device of this invention has a practical advantage that it may be put into effect by employing known and possibly existing forms of container for catalyst bodies, such as elongated tubes, cylinders, spheres, cones or drums. Both radial and axial catalytic converters may be used. The catalyst bodies employed in the invention may be fabricated with dimensions appropriate for use in known containers. They may be placed into a container in such a manner that either initially, or after a period of time, they adopt the abovementioned pre-determined orientation. Devices of the invention do not suffer from serious attrition problems since catalytically active material carried by the walls defining the channels of a particular catalyst body is protected from contact with any other catalyst body in the device, i.e., a significant part of the surface area of the catalyst body lies within a mechanically hard and resistant protective external boundary and is thus protected from attrition.

By "fluid" in this specification is meant fluid containing or consisting of either the reactant or reactants for the reaction to be catalysed or the product or products of such reaction depending upon the context. The fluid may be a gas or a vapour or a liquid.

The catalyst bodies in a particular device of the invention may have substantially similar internal dimensions, e.g. in terms of size, density and/or arrangement of channels. In some applications, however, a device of the invention contains catalyst bodies which are not all of the same internal dimensions. In this way catalytic efficiency may be enhanced by providing greater opportunity for reactants passing through the device to contact catalytically active material. Also, such variation of the internal dimensions of the catalyst bodies of a device may allow reactivity in different parts of the device to be controlled thereby allowing more precise control of temperature profiles to be affected.

By plurality of catalyst bodies in a device of the invention is meant a number such that the catalytic efficiency of the device is greater than that of a device of the same dimensions having a single catalyst body packed in the container, wherein the single body occupies the same proportion of the volume of the device as the catalyst bodies in the device of the invention, has the same internal channel size and arrangement as said bodies and has the same surface coating as said bodies.

In one embodiment of the invention where the bodies are assembled in an orientation comprising one train only and where they have substantially similar internal dimensions, it is most unlikely that the channels of a particular body are precisely aligned with the channels of the next adjacent body (or bodies) in the device. (This assumes deliberate steps are not taken in assembling the device to provide such alignment.)

Thus, in a device having a large number of such bodies, there will be significant non-alignment with channels of adjacent bodies. The catalytic efficiency of the device is thereby enhanced in these circumstances in that a greater degree of mixing of reactants is provided in comparison with the above mentioned device where a single catalyst body only is present.

The requirement in the invention as claimed for the catalyst bodies to "occupy" the cross-section of the container is to minimise the incidence of a fluid reactant or reactants "by-passing" the catalytically active material. The internal walls of the container may, however, also carry a surface coating comprising catalytically active material in order to further minimise "by-passing". In the embodiment of the invention where the bodies are assembled in an orientation comprising one train only, each catalyst body may have external dimensions less than the internal dimensions of the container, for example, in order to prevent binding of the bodies to the container and to assist removal of the bodies from the container. In such circumstances, the disposition of a particular body with respect to the container need not necessarily be the same as that of an adjacent or adjacent bodies. Such a difference in dimensions, if provided, is dictated by the difference in the coefficients of expansion of the container and of the bodies, and also by the likelihood of fouling occurring during use. Where the bodies and the container are each cylindrical in shape, the difference between the external diameter of the bodies and the internal diameter of the container may, for example, be in the range of 0.05 cm to 0.4 cm. Furthermore, where it is desired to minimise contact between the container and the bodies, spacers may be provided, for example mounted either on the container or on the bodies.

In other embodiments of the device the bodies may be assembled in orientations such that a number of trains pass through any cross section of the container chosen to be perpendicular to the general direction of fluid flow at that point.

Mass transfer in the device may be enhanced by using catalyst bodies of short length. In the embodiment of the invention where there is a single train only, natural irregularities in the catalyst body surface perpendicular to the principal axis of the container will usually be sufficient to allow radial mass transfer between catalyst bodies to take place. The invention is not, however, limited to devices where each catalyst body is in close or touching contact with the next adjacent catalyst body or bodies. Thus, it may be necessary in some circumstances to control thermal gradients by causing each body to be separated from the next adjacent body or bodies. The word "train" must therefore be construed accordingly. It is further pointed out that "train" should not be taken to imply that each body is necessarily in a fixed connection with the next adjacent body or bodies. "Train" is used merely to indicate the relative spatial disposition of the bodies. "Aligned with" does not necessarily mean that the train or trains are precisely in line with the general direction of flow. Thus, some angular deviation from precise alignment is possible in the invention as will be illustrated hereinafter. In essence the greatest directional component of the train is aligned with the general direction of flow. Also the train or trains may be branched within the above constraints. When there is more than one train in the container, the trains may, for example, be substantially parallel to one another.

It should be noted that not all of the bodies in the container need necessarily be in the form of one or more trains. Thus, a proportion thereof may be present in random arrangement without significantly affecting the catalytic performance of the device.

The bodies may be placed in the container individually or they may be placed therein as a preformed train or trains, where, for example the bodies are fastened together to constitute the train or trains.

Catalyst bodies for use in this invention having a plurality of channels in substantially parallel arrangement with respect to one another may, for example, have from 400 to 4 channels per square centimetre of the portion of the body at right angles to the direction of the channels. Preferably, there are from 200 to 25 such channels per square centimetre in order to maximise surface area and minimise the risk of blockage of the channels when the device is in use.

The principal axis of the container is preferably linear though other container geometries are possible in the practice of the invention. For example, the principal axis of the container may follow an arcuate path, at least in part.

There are a number of advantages in employing the present invention, rather than randomly packing bodies (e.g. of honeycomb form) into a container. The first is that the pressure drop along the container can be considerably reduced if the contents of the container comprise a substantial number of trains aligned with the general direction of the gas flow. A second is that the catalytic activity of the bodies in the reactant fluid can be enhanced if there is this same alignment of trains with the general direction of fluid flow.

One explanation for these phenomena, is that the reactant fluid is more able to pass through the centres of the catalyst bodies if they are aligned with the general direction of the gas flow. Thus more catalytic surface per unit volume of the device is exposed to the reactants, and a higher catalytic activity per catalyst body is obtained.

Another significant advantage is that the voidage in the container can be significantly reduced by non-random packing of the bodies into a container. The voidage is the percentage of volume not occupied by individual catalyst bodies, where the volume of an individual body includes all the volume within the external boundary of the body. Consequently the volume of the channels within a single body is included in the volume of the body for the calculation of voidage.

Unnecessary voidage will lead to an increase in the volume of the device needed to bring about a certain degree of conversion of reactants to products. Alternatively, in some cases, advantages can be taken of the possibility of obtaining a higher degree of conversion from a larger number of bodies contained within the same volume. In addition the presence of unwanted voidage may increase the proportion of reactants to unwanted by-products due to a modification in the ratio of homogeneous to heterogeneous reactions which can occur in the container.

The present invention has application in the catalysis of those processes whose efficiencies are impaired by high pressure drops. Typical processes include those highly exothermic or endothermic reactions which are or can be carried out in tubular containers. Other typical processes include those in which the rate of reaction is partially controlled by diffusion into the catalyst in these reactions, a compromise is often reached between the advantage gained in using small catalyst bodies and the disadvantages of the accompanying rise in pressure drop. Finally there are those reactions where pressure drop is a problem due to the accumulation of solid particles within the voidage of the container either because of catalyst pellet degradation or because of deposition or decomposition within the voidage of some fraction of the fluid entering the container.

Typical processes which fall into one or more of these categories include the steam reforming of hydrocarbons, methanation, the selective and complete oxidation of hydrocarbons, the oxidation of sulphur dioxide to sulphur trioxide, the oxidation of ammonia, hydrodesulphurisation processes, methanol synthesis and the water-gas shift reaction.

The catalyst bodies may be made of a ceramic material or of a metal. Examples of suitable ceramic materials are mullite, cordierite, silicon carbide, silicon nitride and zirconia. Examples of suitable metals are aluminium bearing iron base alloys, aluminium, stainless steels and high Ni content steels. An example of an aluminium bearing iron base alloy has a composition by weight of 10 to 30% Cr, 1 to 10% Al, 0 to 5% C, and the balance Fe. Such alloys are available in the UK under Registered Trade Mark "Fecralloy".

Where resistance to high temperature embrittlement is important such alloys are made within the specification of a composition by weight of up to 20% Cr, 1 to 10% Al, 0.1 to 3.0% Y and the balance Fe. Where a degree of high temperature embrittlement can be tolerated, higher chromium content up to 25% by weight may be employed. The particularly preferred composition is a Fecralloy (Registered Trade Mark) alloy having 15.50 to 16.50% Cr, 4.6 to 5.6% Al, 0.3 to 1.0% Y and the balance Fe.

The above mentioned alloys may include additions of Co and/or Ni and it is envisaged that such inclusions should be limited to the range of 0 to 3% by weight of each element. However, acceptable performance may be achieved with these additions in the range 0 to 5% Co, and 0 to 5% Ni.

An alternative alloy is that sold under the UK Registered Trade Mark Kanthal Dsd. A typical example of such an alloy has an approximate composition by weight of 22.5% Cr, 4.5% Al, 2.0% Co, 0.1% C and the balance Fe.

A catalyst body of ceramic material for use in the invention may be fabricated by methods known in the art and may, for example, be fabricated with a honeycomb structure for use in the invention. A catalyst body of metal for use in the invention may be fabricated, at least in part, of corrugated metal defining the channels through the body. For example, a metal catalyst body for use in the invention may comprise spirally wound alternate plain and corrugated sheets wound in 'Swiss-roll' type fashion. Such a body may be held together by an suitable externally applied fastening means such as wire, a split ring or a washer, or by welding. Spot or line welding are preferred since they effect a permanent fastening and do not substantially disturb the profile of the bodies. This enables the bodies to fit tightly into the container thereby minimising generation of 'dead' volume in the device.

The surface coating on the catalyst bodies may comprise one or more transition metal elements or a compound thereof as the catalytically active material, for example the metals Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Au and the oxides and mixed oxides of V, Cr, Mo, W and Mn. The choice of catalytically active material is in practice determined to a large extent by the reaction to be treated by catalysis. Preferably, the catalytically active material is supported by a ceramic coating, for example, a refractory oxide coating such as Al_{203}, Ce_{02}, Y_{203}, Ti_{02}, Zr_{02}, Th_{02} and Si_{02}. Such coatings may be applied by methods known in the art, for example, as described in UK Patent Specification No. 1 568 861.

In the production of the catalyst bodies, catalytically active material may be applied by methods known in the art, for example by solution impregnation followed by decomposition, sputtering, plasma coating, flame spraying, vapour deposition or sintering.

In a further aspect the invention provides a method of catalysis of a chemical reaction which comprises passing a reactant or reactants for the reaction through a device according to the invention under conditions for the catalytically active material to effect catalysis of the reaction.

Several ways of carrying out the invention will now be described, by way of example only, as follows where reference will be made to Figures 1 to 7 of the accompanying drawings wherein

Figure 1 is a side view in median section of a catalyst device for the catalysis of chemical reactions involving fluids;

Figure 2 is an enlarged section on the line A—A in Figure 1,

Figures 3 to 6 are schematic side views of catalyst devices for the catalysis of chemical

reactions involving fluids showing various orientations of catalyst bodies; and

Figure 7 is a graph showing the relationship between pressure drop and flow rate for a catalyst device of the invention and for catalyst devices not forming part of the invention.

Referring to Figure 1, a container 1, comprises a central cylindrical portion 2 and a lower end portion 3 and an upper end portion 4. The lower end portion 3 carries an inlet pipe 5 for conveying fluids to the container 1 and the upper end portion 4 carries an outlet pipe 6 for conveying fluids from the container 1. The container 1 carries a single train 7 comprising a plurality of catalyst bodies 8 of generally cylindrical shape packed within the container 1 so that each body 8 fills the cross-section of the container. Each body 8 is in touching contact with the next adjacent body or bodies 8 via its generally flat side or sides.

Referring to Figure 2, a catalyst body 8 is shown in more detail in position in the container 1. Each body 8 comprises alternate plain sheets 9 and corrugated sheets 10 spirally wound in a coil in 'Swiss-roll' type fashion. Each of the sheets 9 and 10 is fabricated of metal. The outer plain sheet (9') constitutes an external protective body (8). The coil is prevented from unwinding by means of a weld (not shown). The sheets 9 and 10 define a plurality of passageways 12 extending through the catalyst body 8. The sheets 9 and 10 each carry a layer of a carrier material (not shown), which in turn carries a layer of a catalytically active material (not shown).

In operation of the device shown in Figure 1, fluid reactants are passed via the inlet pipe 5 into the container 1 in the direction shown by the arrow *a*. The reactants pass through the train 7 and hence through the passageways 12 in the catalyst bodies 8 thereby contacting the catalytically active material (not shown) which catalyses a chemical reaction in the reactants. A product of the chemical reaction issues from the container 1 via the outlet pipe 6 in the direction shown by the arrow *b*. The arrows *a* and *b* indicate the general direction of flow of fluid through the container 1, said general direction including directions parallel to the arrow *a* and *b* within the container 1.

Referring to Figures 3 to 6, each of the figures shows a cylindrical container 1 of similar type to that shown in Figure 1. The container 1 carries inlet and outlet pipes (not shown) similar to those shown in Figure 1. Each container 1 in Figures 3 to 6 carries a plurality of catalyst bodies 8 similar to the catalyst bodies 8 shown in Figures 1 and 2. Only a representative sample of the bodies 8 are shown in the figures. The catalyst bodies 8 are assemblied in an orientation comprising trains 7 thereof. The alignment of some of the trains 7 is indicated in representative cases by dotted lines and each train 7 defines pathways for fluid in the direction of the dotted lines.

In operation of each of the devices shown in Figures 3 to 6, fluid reactants are passed via the inlet pipe (not shown) into the container 1 in the direction shown by the arrow *a*. The reactants pass through the trains 7 and hence through the passageways (not shown) in the catalyst bodies 8 thereby contacting the catalytically active material (not shown) which catalyses a chemical reaction in the reactants. A product of the chemical reaction issues from the container 1 via the outlet pipe (not shown) in the direction shown by the arrow *b*. The arrows *a* and *b* indicate the general direction of flow of fluid through the container 1. Thus, the trains 7 are aligned with said general direction of flow.

In the examples below, Examples 1 and 2 are examples of the invention and Examples A, B and C are comparative examples and are not examples of the invention.

Example 1

A cylindrical container (length 9 cm, diameter 6.5 cm) was packed with 480 cylindrical bodies (length 0.9 cm diameter, 0.85 cm depth of corrugations 1 mm) of the type shown in Figures 1 and 2 herein and fabricated of "Fecralloy" steel. The bodies were packed wholly in the form of the linear trains aligned with the principal axis of the container and substantially parallel to one another. Measurements were made of the voidage (dead space) in the container as a fraction of the total volume of the container and of the pressure drop as a function of air flow rate through the container in the general direction of the principal axis of the container.

Example A

The procedure of Example 1 was repeated with the exception that the catalyst bodies were randomly packed in the container.

Example B

The procedure of Example 1 was repeated with the exception that the catalyst bodies were randomly packed in the container and then vibrated.

Example C

The procedure of Example 1 was repeated with the exception that the catalyst bodies were packed in the container in the form of trains, none of which was aligned with the principal axis of the container.

The voidage results are depicted below

Example	*Voidage (fraction)*
1	0.18
A	0.33
B	0.32
C	0.32

x: Example, 1, Δ: Example A, O: Example B and □: Example C. It is seen the device of Example 1 permits a much higher air flow rate for a given pressure drop than the devices of Example A, B and C.

and the pressure drop results are depicted in the graph in Figure 7 where the quantities measure along the axes and their units are indicated on the graph. The symbols on the graph represent values obtained for the devices of the above examples as follows:

Example 2

480 catalyst bodies as used in Example 1 were coated with a nickel-alumina washcoat containing 616 gms/l $Ni(NO_3)_2.6H_{20}$ and 220 gms/l Al_{203}. The coated bodies were dried and then fired in air for 15 minutes at 450°C. After firing, the mass of the washcoat amounted to 12.7% of the original mass of the monoliths bodies. The bodies were then reduced in hydrogen at 550°C for thirty minutes before they were randomly loaded into a container of 6.5 cms internal diameter to form a bed. A further reduction was then carried out at 250°C. During activity measurements gas was fed to the container at a total flow rate of 50 l/min, with a composition of $16N_2$:1 CO:$3H_2$ (H.S.V.=9090h—1). The gas was preheated so that in the absence of carbon monoxide, the centre of the bed reached a temperature of 224°C.

After the activity of the catalyst bodies had been measured, they were withdrawn from the container and then reloaded so that their internal channels were completely aligned with the general direction of the gas flow therethrough. The catalyst bodies were reduced in precisely the same manner as described above prior to the activity tests.

A percentage of the methane in the effluent gas from the container containing aligned catalyst bodies was twice that from the reactor containing randomly packed catalyst bodies. This shows the greater effectiveness of an ordered array compared with a randomly packed array of catalyst bodies. It is expected that the ratio of activities for ordered and randomly packed arrays, will depend upon space velocity, catalyst body diameter to length ratio and overall catalyst body dimensions.

It is possible that the greater activity of the order array, arises from the enhanced penetration of the internal channels of each catalyst body by the reacting gasses.

Claims

1. A device for use in the catalysis of a chemical reaction comprising a container having a fluid inlet thereto, a fluid outlet therefrom and a plurality of discrete catalyst bodies assembled therein, each body carrying a surface coating comprising a catalytically active material for the reaction, in operation of which, fluid passes in a general direction of flow through the container from the inlet to the outlet, wherein each body has a plurality of internal channels of an ordered, pre-determined size and arrangement to permit substantially unrestricted flow of fluid therethrough, each body has an external protective boundary to protect the body from attrition, and the bodies are assembled in a pre-determined orientation comprising one or more trains occupying the cross-section of the container, the or each train and said channels of each body being aligned with said general direction of flow to define pathways for fluid to pass therethrough in said general direction.

2. A device as claimed in claim 1 wherein there is a single train only assembled in the container.

3. A device as claimed in claim 1 wherein there is more than one train assembled in the container substantially parallel to one another and to the principal axis of the container.

4. A device as claimed in any of the preceding claims wherein each catalyst body has a plurality of channels in substantially parallel arrangement with respect to one another and has from 400 to 4 channels per square centimetre of the portion of the body at right angles to the direction of the channels.

5. A device as claimed in claim 4 wherein each body has from 200 to 25 channels per square centimetre.

6. A device as claimed in any of the preceding claims wherein the catalyst bodies are fabricated of metal in the form of spirally wound alternate plain sheets and corrugated sheets.

7. A device as claimed in claim 6 wherein the metal is an aluminium bearing iron base alloy.

8. A device for use in the catalysis of a chemical reaction substantially as described herein with reference to any of Figures 1 to 6.

9. A method of catalysis of a chemical reaction comprising passing a reactant or reactants for the reaction through a device comprising catalyst bodies assembled in a container, wherein the device is a device as claimed in any of the preceding claims.

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